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Water-soluble surface treating agents

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Inventor(s): ASAI MITSUO (JP); ICHINOHE SHOJI (JP); MATSUMURA KAZUYUKI (JP)
Applicant(s): SHINETSU CHEMICAL CO (JP)
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Abstract

A surface treating agent comprising a reaction product of (A) a fluoroalkyl group-containing alkoxysilane with (B) an amino group-containing alkoxysilane and optionally further with (C) an alkyl group-containing alkoxysilane is water soluble. The agent is diluted with water to form a solution for treating glass and other substrates to impart durable water repellency and other improved properties to the substrates.

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(54) Water-soluble surface treating agents

Wasserlösliches Oberflächenbehandlungsmittel

Agents de traitement de surface solubles dans l'eau

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(73) Proprietor: **SHIN-ETSU CHEMICAL CO., LTD.**
Chiyoda-ku Tokyo (JP)

(72) Inventors:

- **Matsumura, Kazuyuki,**
c/o Shin-Etsu Chem. Co., Ltd.
Usui-gun, Gunma-ken (JP)
- **Asai, Mitsuo, c/o Shin-Etsu Chem. Co., Ltd.**
Usui-gun, Gunma-ken (JP)

- **Ichinohe, Shoji, c/o Shin-Etsu Chem. Co., Ltd.**
Usui-gun, Gunma-ken (JP)

(74) Representative: **Stoner, Gerard Patrick et al**
MEWBURN ELLIS
York House
23 Kingsway
London WC2B 6HP (GB)

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Description

[0001] This invention relates to water-soluble surface treating agents, their preparation and use. Use is proposed with substrates such as glass, inorganic materials, ceramics, metals, and plastics. Desired properties of the treated surface are selectable from water repellent, oil repellent, moisture-proof, stain-proof, anti-icing, lubricant, mould release, weather resistant, and durability properties.

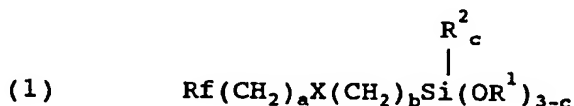
[0002] The current mainstream surface treating agents for glass to form durably water repellent coatings contain as an active ingredient fluoroalkyl group-containing silanes which are diluted with organic solvents. Agents of the solvent dilution type are full of hazards including fire, explosion, poisoning, and environmental pollution. From the aspects of protection of the global environment and utilization of resources too, there is a strong demand for an organic solvent-free surface treating agent for glass, especially a water-soluble surface treating agent for glass.

[0003] Some water soluble surface treating agents are known in the art. For example, EP-A-548775 discloses a surface treating agent comprising a fluoroalkoxysilane and an alkoxysilane, and US-A-2,814,572 discloses a glass surface treating agent comprising a water-soluble organo-silicon compound. The compound disclosed in US-A-2,814,572 is diluted with water to form a transparent mixture. The agent must be used within one day after dilution since the mixture is poor in shelf stability due to rapid polymerization reaction. Water repellency is low since a long chain alkyl group is the only water repellent component.

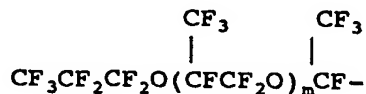
[0004] The aim herein is to provide new and useful surface treating agents, preferably with enhanced properties such as shelf stability water repellency and durability, as well as methods of preparation and use thereof.

[0005] We have found that a reaction product of (A) a fluoroalkyl group-containing alkoxysilane of the general formula (1) and/or its partial hydrolysate with (B) an amino group-containing alkoxysilane of the general formula (2) and/or its partial hydrolysate, and a reaction product of components (A) and (B) with an alkyl group-containing alkoxysilane of the general formula (3) and/or its partial hydrolysate, (formulae shown below) are effective as active ingredients for a surface treating agent. These reaction products are designed so as to impart water solubility to a fluoroalkyl group-containing silane compound which is in itself effective as a water repellent component. Since the reaction products are soluble in water, we find that such surface treating agents can be stable during shelf storage. We also find good properties such as water repellency, and formation of durable coatings.

Formula (1):



[0006] In formula (1), R_f is C_nF_{2n+1} or a polyfluoroalkyl group represented by



wherein n is an integer of 1 to 20 and m is an integer of at least 1, which may have at least one ether bond,

X is at least one linkage group selected from the class consisting of $-CH_2-$, $-CH_2O-$, $-NR^3-$, $-CO_2-$, $-CONR^3-$, $-S-$, $-SO_3-$, and $-SO_2NR^3-$ wherein R^3 is a hydrogen atom or alkyl group of 1 to 8 carbon atoms,

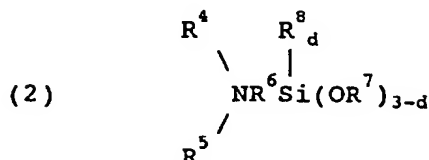
R^1 is an alkyl group having 1 to 4 carbon atoms,

R^2 is an alkyl group having 1 to 4 carbon atoms,

letter a is an integer of 0 to 3, b is an integer of 1 to 3, and c is equal to 0 or 1.

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Formula (2):

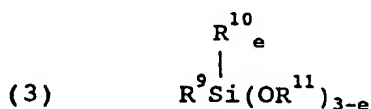


[0007] In formula (2), R^4 and R^5 are independently selected from the class consisting of a hydrogen atom, alkyl group having 1 to 15 carbon atoms, and aminoalkyl group having 1 to 15 carbon atoms,

R^6 is a divalent hydrocarbon group having 1 to 18 carbon atoms,

R^7 is an alkyl group having 1 to 4 carbon atoms,

R^8 is an alkyl group having 1 to 4 carbon atoms, and letter d is equal to 0 or 1. Formula (3):



[0008] In formula (3), R^9 is a monovalent hydrocarbon group having 1 to 10 carbon atoms,

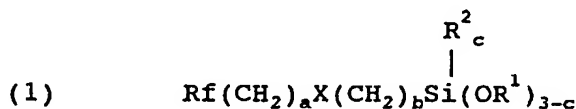
R^{10} is an alkyl group having 1 to 4 carbon atoms,

R^{11} is an alkyl group having 1 to 4 carbon atoms, and letter e is equal to 0 or 1.

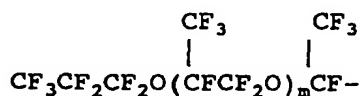
[0009] Therefore, the present invention provides a water-soluble surface treating agent comprising a reaction product of components (A) and (B) or a reaction product of components (A), (B), and (C) and water.

FURTHER EXPLANATIONS; PREFERRED AND OPTIONAL FEATURES

[0010] The water-soluble surface treating agent of the invention is described in more detail. Component (A) is a fluoroalkyl group-containing alkoxysilane of the general formula (1).



[0011] In formula (1), R_f is C_nF_{2n+1} or a polyfluoroalkyl group represented by

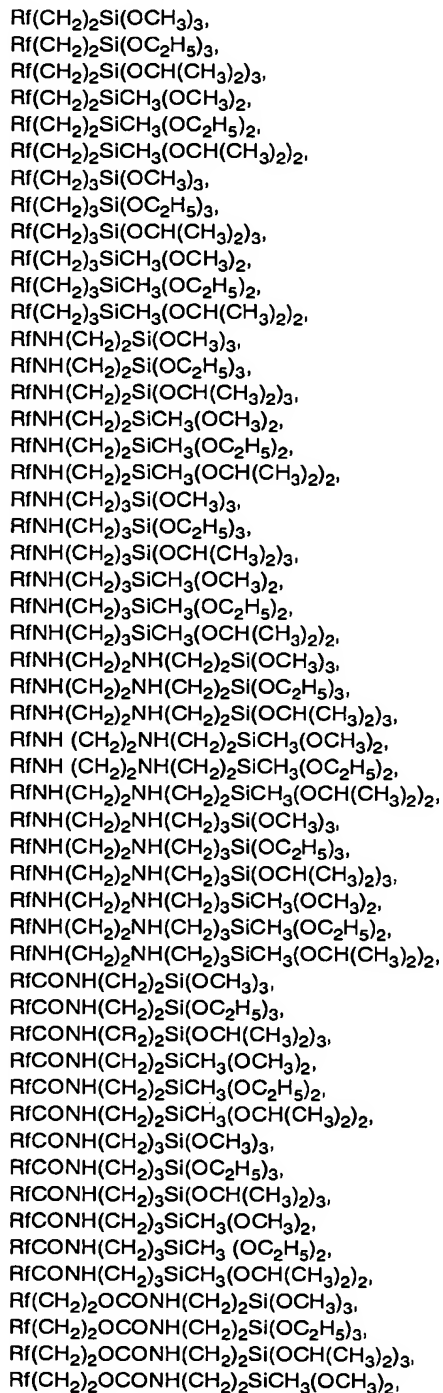


wherein n is an integer of 1 to 20, preferably 1 to 10 and m is an integer of at least 1, preferably 1 to 20, more preferably 1 to 10, which may have at least one ether bond. X is at least one linkage group selected from the class consisting of $-CH_2-$, $-CH_2O-$, $-NR^3-$, $-CO_2-$, $-CONR^3-$, $-S-$, $-SO_3-$, and $-SO_2NR^3-$ wherein R^3 is a hydrogen atom or alkyl group of 1 to 8 carbon atoms. Where X is more than one such group, they are bonded to form a divalent linkage group. R^1 is an alkyl group having 1 to 4 carbon atoms. R^2 is an alkyl group having 1 to 4 carbon atoms. Methyl and ethyl are preferred

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for R¹ and R². Letter a is an integer of 0 to 3, b is an integer of 1 to 3, and c is equal to 0 or 1, preferably 0. Usually X is not more than 6 said linkage groups.

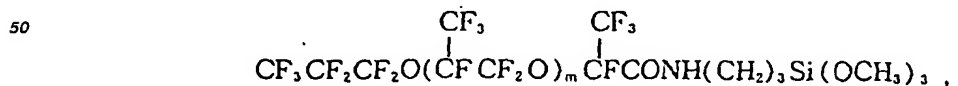
[0012] Illustrative, non-limiting, examples of the fluoroalkyl group-containing alkoxy silane are given below. In the following formulae, Rf is C_nF_{2n+1} wherein n is an integer of 1 to 20, for example, CF₃⁻, C₂F₅⁻, C₃F₇⁻, C₄F₉⁻, C₆F₁₃⁻, C₈F₁₇⁻, C₁₀F₂₁⁻, C₁₂F₂₅⁻, C₁₄F₂₉⁻, C₁₆F₃₃⁻, C₁₈F₃₇⁻, and C₂₀F₄₁⁻.



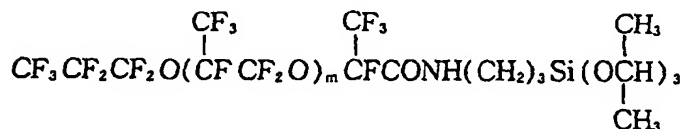
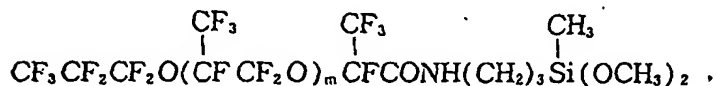
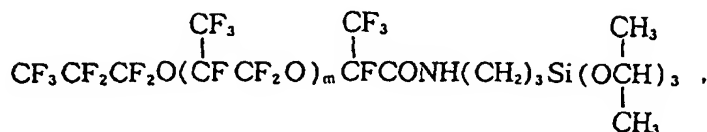
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$\text{Rf}(\text{CH}_2)_2\text{OCONH}(\text{CH}_2)_2\text{SiCH}_3(\text{OC}_2\text{H}_5)_2,$
 $\text{Rf}(\text{CH}_2)_2\text{OCONH}(\text{CH}_2)_2\text{SiCH}_3(\text{OCH}(\text{CH}_3)_2)_2,$
 $\text{Rf}(\text{CH}_2)_2\text{OCONH}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3,$
 $\text{Rf}(\text{CH}_2)_2\text{OCONH}(\text{CH}_2)_3\text{Si}(\text{OC}_2\text{H}_5)_3,$
5 $\text{Rf}(\text{CH}_2)_2\text{OCONH}(\text{CH}_2)_3\text{Si}(\text{OCH}(\text{CH}_3)_2)_3,$
 $\text{Rf}(\text{CH}_2)_2\text{OCONH}(\text{CH}_2)_3\text{SiCH}_3(\text{OCH}_3)_2,$
 $\text{Rf}(\text{CH}_2)_2\text{OCONH}(\text{CH}_2)_3\text{SiCH}_3(\text{OC}_2\text{H}_5)_2,$
 $\text{Rf}(\text{CH}_2)_2\text{OCONH}(\text{CH}_2)_3\text{SiCH}_3(\text{OCH}(\text{CH}_3)_2)_2,$
 $\text{RfSO}_2\text{NH}(\text{CH}_2)_2\text{Si}(\text{OCH}_3)_3,$
10 $\text{RfSO}_2\text{NH}(\text{CH}_2)_2\text{Si}(\text{OC}_2\text{H}_5)_3,$
 $\text{RfSO}_2\text{NH}(\text{CH}_2)_2\text{Si}(\text{OCH}(\text{CH}_3)_2)_3,$
 $\text{RfSO}_2\text{NH}(\text{CH}_2)_2\text{SiCH}_3(\text{OCH}_3)_2,$
 $\text{RfSO}_2\text{NH}(\text{CH}_2)_2\text{SiCH}_3(\text{OC}_2\text{H}_5)_2,$
 $\text{RfSO}_2\text{NH}(\text{CH}_2)_2\text{SiCH}_3(\text{OCH}(\text{CH}_3)_2)_2,$
15 $\text{RfSO}_2\text{NH}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3,$
 $\text{RfSO}_2\text{NH}(\text{CH}_2)_3\text{Si}(\text{OC}_2\text{H}_5)_3,$
 $\text{RfSO}_2\text{NH}(\text{CH}_2)_3\text{Si}(\text{OCH}(\text{CH}_3)_2)_3,$
 $\text{RfSO}_2\text{NH}(\text{CH}_2)_3\text{SiCH}_3(\text{OCH}_3)_2,$
 $\text{RfSO}_2\text{NH}(\text{CH}_2)_3\text{SiCH}_3(\text{OC}_2\text{H}_5)_2,$
20 $\text{RfSO}_2\text{NH}(\text{CH}_2)_3\text{SiCH}_3(\text{OCH}(\text{CH}_3)_2)_2,$
 $\text{RfSO}_2\text{N}(\text{CH}_3)(\text{CH}_2)_2\text{Si}(\text{OCH}_3)_3,$
 $\text{RfSO}_2\text{N}(\text{CH}_3)(\text{CH}_2)_2\text{Si}(\text{OC}_2\text{H}_5)_3,$
 $\text{RfSO}_2\text{N}(\text{CH}_3)(\text{CH}_2)_2\text{Si}(\text{OCH}(\text{CH}_3)_2)_3,$
 $\text{RfSO}_2\text{N}(\text{CH}_3)(\text{CH}_2)_2\text{SiCH}_3(\text{OCH}_3)_2,$
25 $\text{RfSO}_2\text{N}(\text{CH}_3)(\text{CH}_2)_2\text{SiCH}_3(\text{OC}_2\text{H}_5)_2,$
 $\text{RfSO}_2\text{N}(\text{CH}_3)(\text{CH}_2)_2\text{SiCH}_3(\text{OCH}(\text{CH}_3)_2)_2,$
 $\text{RfSO}_2\text{N}(\text{CH}_3)(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3,$
 $\text{RfSO}_2\text{N}(\text{CH}_3)(\text{CH}_2)_3\text{Si}(\text{OC}_2\text{H}_5)_3,$
 $\text{RfSO}_2\text{N}(\text{CH}_3)(\text{CH}_2)_3\text{Si}(\text{OCH}(\text{CH}_3)_2)_3,$
30 $\text{RfSO}_2\text{N}(\text{CH}_3)(\text{CH}_2)_3\text{SiCH}_3(\text{OCH}_3)_2,$
 $\text{RfSO}_2\text{N}(\text{CH}_3)(\text{CH}_2)_3\text{SiCH}_3(\text{OC}_2\text{H}_5)_2,$
 $\text{RfSO}_2\text{N}(\text{CH}_3)(\text{CH}_2)_3\text{SiCH}_3(\text{OCH}(\text{CH}_3)_2)_2,$
 $\text{RfSO}_2\text{NH}(\text{CH}_2)_2\text{CONH}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3,$
 $\text{RfSO}_2\text{NH}(\text{CH}_2)_2\text{CONH}(\text{CH}_2)_3\text{Si}(\text{OC}_2\text{H}_5)_3,$
35 $\text{RfSO}_2\text{NH}(\text{CH}_2)_2\text{CONH}(\text{CH}_2)_3\text{Si}(\text{OCH}(\text{CH}_3)_2)_3,$
 $\text{RfSO}_2\text{NH}(\text{CH}_2)_2\text{CONH}(\text{CH}_2)_3\text{SiCH}_3(\text{OCH}_3)_2,$
 $\text{RfSO}_2\text{NH}(\text{CH}_2)_2\text{CONH}(\text{CH}_2)_3\text{SiCH}_3(\text{OC}_2\text{H}_5)_2,$
 $\text{RfSO}_2\text{NH}(\text{CH}_2)_2\text{CONH}(\text{CH}_2)_3\text{SiCH}_3(\text{OCH}(\text{CH}_3)_2)_2,$
 $\text{RfSO}_2\text{NH}(\text{CH}_2)_3\text{CONH}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3,$
40 $\text{RfSO}_2\text{NH}(\text{CH}_2)_3\text{CONH}(\text{CH}_2)_3\text{Si}(\text{OC}_2\text{H}_5)_3,$
 $\text{RfSO}_2\text{NH}(\text{CH}_2)_3\text{CONH}(\text{CH}_2)_3\text{Si}(\text{OCH}(\text{CH}_3)_2)_3,$
 $\text{RfSO}_2\text{NH}(\text{CH}_2)_3\text{CONH}(\text{CH}_2)_3\text{SiCH}_3(\text{OCH}_3)_2,$
 $\text{RfSO}_2\text{NH}(\text{CH}_2)_3\text{CONH}(\text{CH}_2)_3\text{SiCH}_3(\text{OC}_2\text{H}_5)_2,$
45 $\text{RfSO}_2\text{NH}(\text{CH}_2)_3\text{CONH}(\text{CH}_2)_3\text{SiCH}_3(\text{OCH}(\text{CH}_3)_2)_2,$

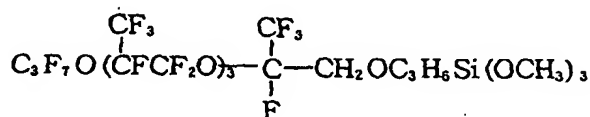
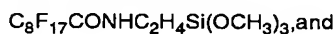
[0013] Thus, possible multigroup X's include $\text{NH}(\text{CH}_2)_2\text{NH}$, OCONH , $\text{SO}_2\text{NR}^3(\text{CH}_2)_2$ or CONH .



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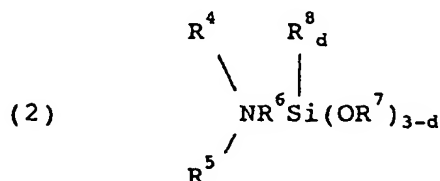
[0014] Preferred among these are the following compounds.



with the first-mentioned one being most preferred.

[0015] In the practice of the invention, not only silanes of formula (1), but also partial hydrolysates of the silanes are useful as component (A) while a mixture of silane and partial hydrolysate is also acceptable. The partial hydrolysate should have at least one hydrolysate group left therein. A mixture of silanes and a mixture of partially hydrolysed silanes may also be used if desired.

[0016] Component (B) is an amino group-containing alkoxysilane of the general formula (2).

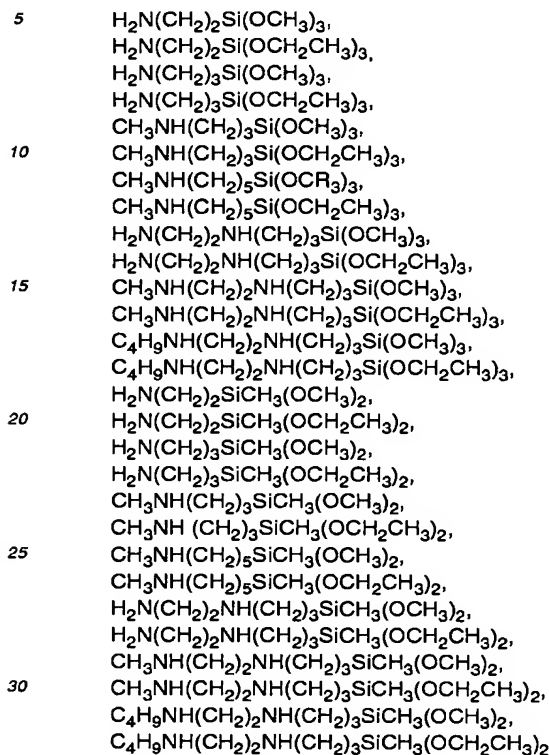


[0017] In formula (2), each of R^4 and R^5 , which may be identical or different, is a hydrogen atom, alkyl group having 1 to 15 carbon atoms, preferably 1 to 4 carbon atoms or aminoalkyl group having 1 to 15 carbon atoms, preferably 1 to 6 carbon atoms. R^6 is a divalent hydrocarbon group having 1 to 18 carbon atoms, preferably 1 to 6 carbon atoms,

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such as alkylene, arylene, and alkylarylene groups. R⁷ is an alkyl group having 1 to 4 carbon atoms. R⁸ is an alkyl group having 1 to 4 carbon atoms. Letter d is equal to 0 or 1.

[0018] Illustrative, non-limiting, examples of the amino group-containing alkoxysilane are given below.



[0019] Preferred among these are N-(2-aminoethyl)-3-aminopropyltrimethoxysilane, N-(2-aminoethyl)-3-aminopropylmethyldimethoxysilane, and 3-aminopropyltrimethoxysilane.

[0020] In the practice of the invention, not only silanes of formula (2), but also partial hydrolysates of the silanes are useful as component (B).

[0021] The water-soluble surface treating agent according to the first aspect contains a reaction product of components (A) and (B) as a main ingredient, which is dissolved in water. The reaction product is obtainable by effecting co-hydrolysis and condensation of components (A) and (B) in the presence of organic or inorganic acids. It is preferred from the stability point of view to produce the reaction product by first effecting partial hydrolysis of component (A) in the presence of an organic or inorganic acid and then reacting the partially hydrolysed component (A) with component (B).

[0022] Examples of the organic or inorganic acid used in hydrolysis of component (A) include hydrochloric acid, sulfuric acid, methanesulfonic acid, formic acid, acetic acid, propionic acid, citric acid, oxalic acid, and maleic acid alone or in admixture, with acetic acid and propionic acid being preferred. The acid is preferably used in an amount of about 5 to 400 parts by weight, more preferably about 15 to 350 parts by weight per 100 parts by weight of component (A). With less than 5 parts of the acid, the progress of hydrolysis would be retarded and the agent in aqueous solution form would be less stable. Most preferably the acid catalyst is added in such an amount that when the reaction product is dissolved in water, the resulting aqueous system may be adjusted at pH 7.0 to 3.0.

[0023] Upon hydrolysis, the reactant is preferably diluted with a solvent. The solvents used herein are preferably alcohol solvents including methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol, and 3-butanol, with the 3-butanol being most preferred. The solvent is preferably used in an amount of about 100 to 500 parts by weight, more preferably about 200 to 400 parts by weight per 100 parts by weight of component (A). Less than 100 parts of the solvent would allow condensation to take place whereas more than 500 parts of the solvent would undesirably retard hydrolysis.

[0024] For hydrolysis, water is preferably added to component (A) in an amount of about 1.0 to 3.0 mol, more preferably 1.2 to 2.5 mol per mol of component (A). Less than 1.0 mol of water would leave much alkoxy groups whereas

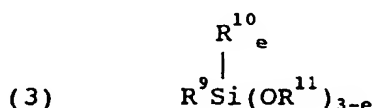
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more than 3.0 mol of water would promote condensation. Preferred reaction conditions include a reaction temperature of 10 to 100°C, preferably 60 to 90°C and a reaction time of about 1 to 3 hours.

[0025] The thus hydrolysed component (A) is then successively reacted with component (B). The molar ratio of components (B) and (A) is from 0.5:1.0 to 20.0:1.0. With a molar ratio of (B)/(A) of less than 0.5/1, water solubility would be low. With a molar ratio of (B)/(A) of more than 20.0/1, water repellency would be low. As to conditions for the reaction of component (B), a reaction temperature of 60 to 100°C and a reaction time of about 1 to 3 hours are preferred.

[0026] The water-soluble surface treating agent according to the second aspect contains a reaction product of the above-mentioned components (A) and (B) and the following component (C) as a main ingredient, which is dissolved in water.

[0027] Component (C) is an alkyl group-containing alkoxysilane of the general formula (3).



[0028] In formula (3), R^9 is a monovalent hydrocarbon group having 1 to 10 carbon atoms, R^{10} is an alkyl group having 1 to 4 carbon atoms, R^{11} is an alkyl group having 1 to 4 carbon atoms, and letter e is equal to 0 or 1. Examples of the monovalent hydrocarbon group include alkyl, alkenyl, aryl, and aralkyl groups and halogen substituted ones thereof, with the alkyl groups being preferred.

[0029] Illustrative, non-limiting, examples of the alkyl group-containing alkoxysilane are given below.

$C_{10}H_{21}Si(OCH_3)_3$,
 $C_{10}H_{21}Si(OC_2H_5)_3$,
 $C_{10}H_{21}Si(OCH(CH_3)_2)_3$,
 $C_{10}H_{21}Si(CH_3)(OCH_3)_2$,
 $C_{10}H_{21}Si(CH_3)(OC_2H_5)_2$,
 $C_{10}H_{21}Si(CH_3)(OCH(CH_3)_2)_2$,
 $C_8H_{17}Si(OCH_3)_3$,
 $C_8H_{17}Si(OC_2H_5)_3$,
 $C_8H_{17}Si(OCH(CH_3)_2)_3$,
 $C_8H_{17}Si(CH_3)(OCH_3)_2$,
 $C_8H_{17}Si(CH_3)(OC_2H_5)_2$,
 $C_8H_{17}Si(CH_3)(OCH(CH_3)_2)_2$,
 $C_6H_{13}Si(OCH_3)_3$,
 $C_6H_{13}Si(OC_2H_5)_3$,
 $C_6H_{13}Si(OCH(CH_3)_2)_3$,
 $C_6H_{13}Si(CH_3)(OCH_3)_2$,
 $C_6H_{13}Si(CH_3)(OC_2H_5)_2$,
 $C_6H_{13}Si(CH_3)(OCH(CH_3)_2)_2$,
 $C_4H_9Si(OCH_3)_3$,
 $C_4H_9Si(OC_2H_5)_3$,
 $C_4H_9Si(OCH(CH_3)_2)_3$,
 $C_4H_9Si(CH_3)(OCH_3)_2$,
 $C_4H_9Si(CH_3)(OC_2H_5)_2$,
 $C_4H_9Si(CH_3)(OCH(CH_3)_2)_2$,
 $C_3H_7Si(OCH_3)_3$,
 $C_3H_7Si(OC_2H_5)_3$,
 $C_3H_7Si(OCH(CH_3)_2)_3$,
 $C_3H_7Si(CH_3)(OCH_3)_2$,
 $C_3H_7Si(CH_3)(OC_2H_5)_2$,
 $C_3H_7Si(CH_3)(OCH(CH_3)_2)_2$,
 $C_2H_5Si(OCH_3)_3$,
 $C_2H_5Si(OC_2H_5)_3$,
 $C_2H_5Si(OCH(CH_3)_2)_3$,
 $C_2H_5Si(CH_3)(OCH_3)_2$

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$C_2H_5Si(CH_3)(OC_2H_5)_2$,
 $C_2H_5Si(CH_3)(OCH(CH_3)_2)_2$,
 $CH_3Si(OCH_3)_3$,
 $CH_3Si(OC_2H_5)_3$,
 $CH_3Si(OCH(CH_3)_2)_3$,
 $(CH_3)_2Si(OCH_3)_2$,
 $(CH_3)_2Si(OC_2H_5)_2$,
 $(CH_3)_2Si(OCH(CH_3)_2)_2$

10 [0030] Preferred among these are $C_{10}H_{21}Si(OCH_3)_3$, $C_{10}H_{21}Si(CH_3)(OCH_3)_2$, $(CH_3)_2Si(OCH_3)_2$, and $(CH_3)_2Si(OC_2H_5)_2$.

[0031] In the practice of the invention, not only silanes of formula (3) but also partial hydrolysates of the silanes are useful as component (C).

15 [0032] The reaction product of components (A), (B) and (C) is obtainable by effecting co-hydrolysis and condensation of components (A), (B) and (C) in the presence of organic or inorganic acids. It is preferred from the stability point of view to produce the reaction product by first effecting partial hydrolysis of components (A) and (C) in the presence of an organic or inorganic acid and then reacting the partially hydrolysed components (A) and (C) with component (B).

[0033] Examples of the organic or inorganic acid used in hydrolysis of components (A) and (C) include hydrochloric acid, sulfuric acid, methanesulfonic acid, formic acid, acetic acid, propionic acid, citric acid, oxalic acid, and maleic acid alone or in admixture, with acetic acid and propionic acid being preferred. The acid is preferably used in an amount of about 30 to 400 parts by weight, more preferably about 40 to 350 parts by weight per 100 parts by weight of components (A) and (C) combined. With less than 30 parts of the acid, the progress of hydrolysis would be retarded and the agent in aqueous solution form would be less stable. Most preferably the acid catalyst is added in such an amount that when the reaction product is dissolved in water, the resulting aqueous system may be adjusted at pH 7.0 to 3.0.

25 [0034] Upon hydrolysis, the reactants are preferably diluted with a solvent. The solvents used herein are preferably alcohol solvents including methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol, 3-butanol, and 2-methyl-2-butanol, with the 3-butanol being most preferred. The solvent is preferably used in an amount of about 100 to 500 parts by weight, more preferably about 200 to 400 parts by weight per 100 parts by weight of components (A) and (C) combined. Less than 100 parts of the solvent would allow condensation to take place whereas more than 500 parts of the solvent would undesirably retard hydrolysis.

[0035] For hydrolysis, water is preferably added to components (A) and (C) in an amount of about 1 to 3 mol, more preferably 1.2 to 2.5 mol per mol of components (A) and (C) combined. Less than 1 mol of water would leave much alkoxy groups whereas more than 3 mol of water would promote condensation. Preferred reaction conditions include a reaction temperature of 10 to 100°C, preferably 60 to 90°C and a reaction time of about 1 to 3 hours.

35 [0036] The molar ratio of components (C) and (A) is from 0.05:1 to 0.5:1. With a molar ratio of (C)/(A) of less than 0.05/1, durability would be low. With a molar ratio of (C)/(A) of more than 0.5/1, water solubility and/or oil repellency would be low.

[0037] The thus hydrolysed product of components (A) and (C) is then successively reacted with component (B). The molar ratio of component (B) to components (A) and (C) combined is from 0.5:1 to 20:1. With a molar ratio of (B)/(A + C) of less than 0.5/1, water solubility would be low. With a molar ratio of (B)/(A + C) of more than 20/1, water repellency would be low. As to conditions for the reaction of component (B), a reaction temperature of 60 to 100°C and a reaction time of about 1 to 3 hours are preferred.

[0038] The water-soluble surface treating agent may be used by diluting with water such that e.g. the concentration of water may be 99.9 to 90% by weight, more preferably 99 to 97% by weight. With a water concentration of more than 99.9% by weight, it may be difficult to take advantage of the reaction product and an excessively large amount of the dilution must be applied. A water concentration of less than 90% by weight may sometimes lead to shelf instability.

[0039] To the water-soluble surface treating agent of the invention, surfactants and well-known additives such as alcohols may be added for improving substrate wettability and aqueous solution stability insofar as the objects of the invention are not impaired. Metal base curing catalysts such as Al, Sn and Zn may also be added if desired.

50 [0040] The water-soluble surface treating agents disclosed herein may be applied to substrates of glass, inorganic materials, ceramics, metals or plastics for imparting thereto water repellent, oil repellent, moisture-proof, stain-proof, anti-icing, lubricant, mold release, weather resistant, and durable properties. The substrates can be treated with the agent by well-known techniques such as coating, dipping, and spraying. The agent will find use as water repellent agents, oil repellent agents, moisture-proof agents, anti-icing agents, anti-staining agents, lubricants, and mold release agents. More specifically, the agent is useful for the purposes of moisture-proof treatment of electronic parts, anti-staining surface treatment of optical lenses, moisture-proof, anti-staining, and lubricating surface treatment of optical and magnetic recording media, anti-staining surface treatment of liquid crystal displays and CRT displays, anti-staining and moisture-proof treatment of transparent plastic parts such as optical disc pickups, water-repellent and anti-icing

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surface treatment of glass and plastic glazing in automobiles, trains, aircraft, and helicopters, water-repellent and anti-staining surface treatment of building glazing, water-repellent and anti-icing surface treatment of radar antennas, TV antennas, and roofing, mold release treatment of molds for plastic molding, anti-staining treatment of electronic parts and precision equipment against lubricating oil, and water-repellent and lubricating wet treatment of oxides such as silica and titanium oxide.

EXAMPLE

[0041] Examples of the invention are given below by way of illustration and not by way of limitation.

Synthesis Example 1

[0042] A 1.0-liter four-necked flask equipped with a stirrer, condenser, thermometer, and dropping funnel was charged with 100 grams (0.176 mol) of $C_8F_{17}(CH_2)_2Si(OCH_3)_3$, 340 grams of 3-butanol, 26.3 grams (0.438 mol) of acetic acid, and 4.75 grams (0.264 mol) of water. With stirring, the flask was heated until 3-butanol refluxed. Reaction was continued for 2 hours in this condition. To the flask, 39.1 grams (0.176 mol) of $H_2N(CH_2)_2HN(CH_2)_3Si(OCH_3)_3$ was added dropwise. Reaction was continued for a further 1 hour under reflux of 3-butanol, obtaining a pale yellow clear liquid.

Synthesis Example 2

[0043] The procedure of Synthesis Example 1 was repeated except that 34.8 grams (0.58 mol) of acetic acid and 78.1 grams (0.352 mol) of $H_2N(CH_2)_2HN(CH_2)_3Si(OCH_3)_3$ were used. There was obtained a pale yellow clear liquid.

Synthesis Example 3

[0044] The procedure of Synthesis Example 1 was repeated except that methanol was used instead of the 3-butanol. Thereafter, the reaction solution was heated at 110°C to distill off the methanol, obtaining a yellow white viscous product.

Synthesis Example 4

[0045] The procedure of Synthesis Example 2 was repeated except that methanol was used instead of the 3-butanol. Thereafter, the reaction solution was heated at 110°C to distill off the methanol, obtaining a yellow white viscous product.

Synthesis Example 5

[0046] The procedure of Synthesis Example 1 was repeated except that 36.3 grams (0.176 mol) of $H_2N(CH_2)_2HN(CH_2)_3Si(OCH_3)_3$ was used instead of $H_2N(CH_2)_2HN(CH_2)_3Si(OCH_3)_3$. There was obtained a pale yellow clear liquid.

Synthesis Example 6

[0047] The procedure of Synthesis Example 1 was repeated except that 15.8 grams (0.264 mol) of acetic acid was used and 31.5 grams (0.176 mol) of $H_2N(CH_2)_3Si(OCH_3)_3$ was used instead of $H_2N(CH_2)_2HN(CH_2)_3Si(OCH_3)_3$. There was obtained a clear liquid.

Synthesis Example 7

[0048] The procedure of Synthesis Example 1 was repeated except that 107.5 grams (0.176 mol) of $C_8F_{17}CONH(CH_2)_2Si(OCH_3)_3$ was used instead of $C_8F_{17}(CH_2)_2Si(OCH_3)_3$. There was obtained a pale yellow clear liquid.

Synthesis Example 8

[0049] A 1.0-liter four-necked flask equipped with a stirrer, condenser, thermometer, and dropping funnel was charged with 129.2 grams (0.33 mol) of $C_{18}H_{37}SiCl_3$ and 200 grams of methylene chloride. With stirring, 89 grams (1.0 mol) of 2-dimethylaminoethanol diluted with 100 grams of methylene chloride was added dropwise to the flask from the dropping funnel. At the end of addition, 670 grams of 3-butanol was added to the contents, which were further stirred. The reaction solution was heated at 80°C to distill off the methylene chloride. After cooling, 60 grams (1.0 mol) of acetic acid was added to the contents, which were stirred. Upon filtration, there was obtained a pale yellow clear liquid.

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Synthesis Example 9

[0050] A 1.0-liter four-necked flask equipped with a stirrer, condenser, thermometer, and dropping funnel was charged with 100 grams (0.172 mol) of $C_8F_{17}C_2H_4SiCl_3$ and 152 grams of hexane. With stirring, 46 grams (0.516 mol) of 2-dimethylaminoethanol diluted with 23 grams of hexane was added dropwise to the flask from the dropping funnel. At the end of addition, the contents were stirred for 1 hour and 358 grams of 3-butanol was added to the contents, which were further stirred. The reaction solution was heated at 80°C to distill off the hexane. After cooling, 32 grams (0.53 mol) of acetic acid was added to the contents, which were stirred. Upon filtration, there was obtained a pale yellow clear liquid.

Synthesis Example 10

[0051] A 1.0-liter four-necked flask equipped with a stirrer, condenser, thermometer, and dropping funnel was charged with 15 grams (0.026 mol) of $C_8F_{17}(CH_2)_2Si(OCH_3)_3$, 735 grams of 2-propanol, and 0.48 grams of 0.01N hydrochloric acid. With stirring, the flask was heated until 2-propanol refluxed. Reaction was continued for 2 hours in this condition, obtaining a clear liquid.

Example 1

[0052] A surface treating agent aqueous solution was prepared by diluting the reaction solution obtained in Synthesis Example 1 with water so that the concentration of its active component was 2% by weight. The solution was allowed to stand at room temperature for one month whereupon no change was observed.

[0053] Glass plates of 70 mm x 150 mm x 3 mm thick were dipped for 5 minutes in the solution both immediately after preparation and after aging at room temperature for one week. The treated glass plates were washed with water and heated at 100°C for 15 minutes. These samples were examined for water repellency by measuring a contact angle with water. The results are shown in Table 1.

(a) Contact angle

[0054] A contact angle of a sample with water was measured. Measurement was done at five different points on the substrate surface. With maximum and minimum measurements cut off, an average of the remaining measurements was calculated.

(b) Boiling test

[0055] A sample was dipped in boiling water for 1 hour before its contact angle with water was measured by the same procedure as above.

Example 2

[0056] A surface treating agent aqueous solution was prepared by diluting the reaction solution obtained in Synthesis Example 2 with water so that the concentration of its active component was 2% by weight. The solution was allowed to stand at room temperature for one month whereupon no change was observed.

[0057] Glass plates of 70 mm x 150 mm x 3 mm thick were dipped for 5 minutes in the solution both immediately after preparation and after aging at room temperature for one week. The treated glass plates were washed with water and heated at 100°C for 15 minutes. The test results of these samples are shown in Table 1.

Example 3

[0058] A surface treating agent aqueous solution was prepared by diluting 2 parts by weight of the reaction product obtained in Synthesis Example 3 with 98 parts by weight of water. The solution was allowed to stand at room temperature for one month whereupon no change was observed.

[0059] Glass plates of 70 mm x 150 mm x 3 mm thick were dipped for 5 minutes in the solution both immediately after preparation and after aging at room temperature for one week. The treated glass plates were washed with water and heated at 100°C for 15 minutes. The test results of these samples are shown in Table 1.

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[0060] A surface treating agent aqueous solution was prepared by diluting 2 parts by weight of the reaction product obtained in Synthesis Example 4 with 98 parts by weight of water. The solution was allowed to stand at room temperature for one month whereupon no change was observed.

[0061] Glass plates of 70 mm x 150 mm x 3 mm thick were dipped for 5 minutes in the solution both immediately after preparation and after aging at room temperature for one week. The treated glass plates were washed with water and heated at 100°C for 15 minutes. The test results of these samples are shown in Table 1.

Example 5

[0062] A surface treating agent aqueous solution was prepared by diluting the reaction solution obtained in Synthesis Example 5 with water so that the concentration of its active component was 2% by weight. The solution was allowed to stand at room temperature for one month whereupon no change was observed.

[0063] Glass plates of 70 mm x 150 mm x 3 mm thick were dipped for 5 minutes in the solution both immediately after preparation and after aging at room temperature for one week. The treated glass plates were washed with water and heated at 100°C for 15 minutes. The test results of these samples are shown in Table 1.

Example 6

[0064] A surface treating agent aqueous solution was prepared by diluting the reaction solution obtained in Synthesis Example 6 with water so that the concentration of its active component was 2% by weight. The solution was allowed to stand at room temperature for one month whereupon no change was observed.

[0065] Glass plates of 70 mm x 150 mm x 3 mm thick were dipped for 5 minutes in the solution both immediately after preparation and after aging at room temperature for one week. The treated glass plates were washed with water and heated at 100°C for 15 minutes. The test results of these samples are shown in Table 1.

Example 7

[0066] A surface treating agent aqueous solution was prepared by diluting the reaction solution obtained in Synthesis Example 7 with water so that the concentration of its active component was 2% by weight. The solution was allowed to stand at room temperature for one month whereupon no change was observed.

[0067] Glass plates of 70 mm x 150 mm x 3 mm thick were dipped for 5 minutes in the solution both immediately after preparation and after aging at room temperature for one week. The treated glass plates were washed with water and heated at 100°C for 15 minutes. The test results of these samples are shown in Table 1.

Comparative Example 1

[0068] A surface treating agent aqueous solution was prepared by diluting the reaction solution obtained in Synthesis Example 8 with water so that the concentration of its active component was 2% by weight. The solution became white turbid after it was allowed to stand at room temperature for one day. A glass plate of 70 mm x 150 mm x 3 mm thick was dipped in the solution for 5 minutes, washed with water, and heated at 100°C for 15 minutes. The test results of this sample are shown in Table 1.

Comparative Example 2

[0069] A surface treating agent aqueous solution was prepared by diluting the reaction solution obtained in Synthesis Example 9 with water so that the concentration of its active component was 2% by weight. The solution was white turbid immediately after preparation. A glass plate of 70 mm x 150 mm x 3 mm thick was dipped in the solution for 5 minutes, washed with water, and heated at 100°C for 15 minutes. The test results of this sample are shown in Table 1.

Comparative Example 3

[0070] A surface treating agent aqueous solution was prepared by diluting the reaction solution obtained in Synthesis Example 10 with water so that the concentration of its active component was 2% by weight. A glass plate of 70 mm x 150 mm x 3 mm thick was dipped in the solution for 5 minutes, washed with water, and heated at 100°C for 15 minutes. The test results of this sample are shown in Table 1.

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Table 1

	Contact angle (°)		Contact angle (°) after boiling test	
	Fresh	7 days	Fresh	7 days
Example 1	108	107	103	102
Example 2	107	107	102	102
Example 3	108	106	102	100
Example 4	108	106	101	100
Example 5	108	105	100	101
Example 6	108	107	102	102
Example 7	107	107	102	100
CE 1	80	inapplicable	61	inapplicable
CE 2	93	85	88	79
CE 3	102	100	95	93

Synthesis Example 11

[0071] A 0.5-liter four-necked flask equipped with a stirrer, condenser, thermometer, and dropping funnel was charged with 48.8 grams (0.086 mol) of $C_8F_{17}(CH_2)_2Si(OCH_3)_3$, 1.2 grams (0.009 mol) of $(CH_3)_2Si(OCH_3)_2$, 169 grams of 3-butanol, 14.2 grams (0.237 mol) of acetic acid, and 2.6 grams (0.142 mol) of water. With stirring, the flask was heated until 3-butanol refluxed. Reaction was continued for 2 hours in this condition. To the flask, 21.0 grams (0.095 mol) of $H_2N(CH_2)_2HN(CH_2)_3Si(OCH_3)_3$ was added dropwise. Reaction was continued for a further 1 hour under reflux of 3-butanol, obtaining a pale yellow clear liquid.

Synthesis Example 12

[0072] A 0.5-liter four-necked flask equipped with a stirrer, condenser, thermometer, and dropping funnel was charged with 48.0 grams (0.085 mol) of $C_8F_{17}(CH_2)_2Si(OCH_3)_3$, 2.0 grams (0.017 mol) of $(CH_3)_2Si(OCH_3)_2$, 169 grams of 3-butanol, 15.1 grams (0.253 mol) of acetic acid, and 2.7 grams (0.152 mol) of water. With stirring, the flask was heated until 3-butanol refluxed. Reaction was continued for 2 hours in this condition. To the flask, 22.5 grams (0.101 mol) of $H_2N(CH_2)_2HN(CH_2)_3Si(OCH_3)_3$ was added dropwise. Reaction was continued for a further 1 hour under reflux of 3-butanol, obtaining a pale yellow clear liquid.

Synthesis Example 13

[0073] A 0.5-liter four-necked flask equipped with a stirrer, condenser, thermometer, and dropping funnel was charged with 48.8 grams (0.086 mol) of $C_8F_{17}(CH_2)_2Si(OCH_3)_3$, 1.2 grams (0.009 mol) of $(CH_3)_2Si(OCH_3)_2$, 169 grams of 3-butanol, 8.5 grams (0.142 mol) of acetic acid, and 2.6 grams (0.142 mol) of water. With stirring, the flask was heated until 3-butanol refluxed. Reaction was continued for 2 hours in this condition. To the flask, 16.9 grams (0.095 mol) of $H_2N(CH_2)_2HN(CH_2)_3Si(OCH_3)_3$ was added dropwise. Reaction was continued for a further 1 hour under reflux of 3-butanol, obtaining a clear liquid.

Synthesis Example 14

[0074] The procedure of Synthesis Example 11 was repeated except that 2.3 grams (0.009 mol) of $C_{10}H_{21}Si(OCH_3)_3$ was used instead of $(CH_3)_2Si(OCH_3)_2$. There was obtained a pale yellow clear liquid.

Synthesis Example 15

[0075] The procedure of Synthesis Example 11 was repeated except that 1.8 grams (0.009 mol) of $C_6H_{13}Si(OCH_3)_3$ was used instead of $(CH_3)_2Si(OCH_3)_2$. There was obtained a pale yellow clear liquid.

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Synthesis Example 16

[0076] The procedure of Synthesis Example 11 was repeated except that 1.4 grams (0.009 mol) of $C_3H_7Si(OCH_3)_3$ was used instead of $(CH_3)_2Si(OCH_3)_2$. There was obtained a pale yellow clear liquid.

Synthesis Example 17

[0077] The procedure of Synthesis Example 11 was repeated except that 52.5 grams (0.086 mol) of $C_8F_{17}CONH(CH_2)_2Si(OCH_3)_3$ was used instead of $C_8F_{17}(CH_2)_2Si(OCH_3)_3$. There was obtained a pale yellow clear liquid.

Synthesis Example 18

[0078] The procedure of Synthesis Example 11 was repeated except that 8.6 grams (0.143 mol) of acetic acid was used and 17.0 grams (0.095 mol) of $H_2N(CH_2)_3Si(OCH_3)_3$ was used instead of $H_2N(CH_2)_2HN(CH_2)_3Si(OCH_3)_3$. There was obtained a clear liquid.

Example 8

[0079] A surface treating agent aqueous solution was prepared by diluting the reaction solution obtained in Synthesis Example 11 with water so that the concentration of its active component was 2% by weight. The solution was allowed to stand at room temperature for one month whereupon no change was observed.

[0080] Glass plates of 70 mm x 150 mm x 3 mm thick were dipped for 5 minutes in the solution both immediately after preparation and after aging at room temperature for one week. The treated glass plates were air dried at 25°C for 24 hours and wiped with ethanol. These samples were examined for water repellency by measuring a contact angle with water. The results are shown in Table 2.

(a) Contact angle

[0081] A contact angle of a sample with water was measured. Measurement was done at five different points on the substrate surface. With maximum and minimum measurements cut off, an average of the remaining measurements was calculated.

(b) Boiling test

[0082] A sample was dipped in boiling water for 1 hour before its contact angle with water was measured by the same procedure as above.

(c) Wear test

[0083] Using a scratch abrasion tester (manufactured by KNT K.K.), a sample was subject to a fabric abrasion test under a load of 1 kg/cm² for 3,000 cycles. Its contact angle with water was then measured by the same procedure as above.

Example 9

[0084] A surface treating agent aqueous solution was prepared by diluting the reaction solution obtained in Synthesis Example 12 with water so that the concentration of its active component was 2% by weight. The solution was allowed to stand at room temperature for one month, with no change observed.

[0085] Glass plates of 70 mm x 150 mm x 3 mm thick were dipped for 5 minutes in the solution both immediately after preparation and after aging at room temperature for one week. The treated glass plates were air dried at 25°C for 24 hours and wiped with ethanol. The test results of these samples are shown in Table 2.

Example 10

[0086] A surface treating agent aqueous solution was prepared by diluting the reaction solution obtained in Synthesis Example 13 with water so that the concentration of its active component was 2% by weight. The solution was allowed to stand at room temperature for one month, with no change observed.

[0087] Glass plates of 70 mm x 150 mm x 3 mm thick were dipped for 5 minutes in the solution both immediately

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after preparation and after aging at room temperature for one week. The treated glass plates were air dried at 25°C for 24 hours and wiped with ethanol. The test results of these samples are shown in Table 2.

Example 11

[0088] A surface treating agent aqueous solution was prepared by diluting the reaction solution obtained in Synthesis Example 14 with water so that the concentration of its active component was 2% by weight. The solution was allowed to stand at room temperature for one month, with no change observed.

[0089] Glass plates of 70 mm x 150 mm x 3 mm thick were dipped for 5 minutes in the solution both immediately after preparation and after aging at room temperature for one week. The treated glass plates were air dried at 25°C for 24 hours and wiped with ethanol. The test results of these samples are shown in Table 2.

Example 12

[0090] A surface treating agent aqueous solution was prepared by diluting the reaction solution obtained in Synthesis Example 15 with water so that the concentration of its active component was 2% by weight. The solution was allowed to stand at room temperature for one month, with no change observed.

[0091] Glass plates of 70 mm x 150 mm x 3 mm thick were dipped for 5 minutes in the solution both immediately after preparation and after aging at room temperature for one week. The treated glass plates were air dried at 25°C for 24 hours and wiped with ethanol. The test results of these samples are shown in Table 2.

Example 13

[0092] A surface treating agent aqueous solution was prepared by diluting the reaction solution obtained in Synthesis Example 16 with water so that the concentration of its active component was 2% by weight. The solution was allowed to stand at room temperature for one month, with no change observed.

[0093] Glass plates of 70 mm x 150 mm x 3 mm thick were dipped for 5 minutes in the solution both immediately after preparation and after aging at room temperature for one week. The treated glass plates were air dried at 25°C for 24 hours and wiped with ethanol. The test results of these samples are shown in Table 2.

Example 14

[0094] A surface treating agent aqueous solution was prepared by diluting the reaction solution obtained in Synthesis Example 17 with water so that the concentration of its active component was 2% by weight. The solution was allowed to stand at room temperature for one month, with no change observed.

[0095] Glass plates of 70 mm x 150 mm x 3 mm thick were dipped for 5 minutes in the solution both immediately after preparation and after aging at room temperature for one week. The treated glass plates were air dried at 25°C for 24 hours and wiped with ethanol. The test results of these samples are shown in Table 2.

Example 15

[0096] A surface treating agent aqueous solution was prepared by diluting the reaction solution obtained in Synthesis Example 18 with water so that the concentration of its active component was 2% by weight. The solution was allowed to stand at room temperature for one month, with no change observed.

[0097] Glass plates of 70 mm x 150 mm x 3 mm thick were dipped for 5 minutes in the solution both immediately after preparation and after aging at room temperature for one week. The treated glass plates were air dried at 25°C for 24 hours and wiped with ethanol. The test results of these samples are shown in Table 2.

Comparative Example 4

[0098] A surface treating agent aqueous solution was prepared by diluting the reaction solution obtained in Synthesis Example 8 with water so that the concentration of its active component was 2% by weight. The solution became white turbid after it was allowed to stand at room temperature for 1 day. A glass plate of 70 mm x 150 mm x 3 mm thick was dipped in the solution for 5 minutes, air dried at 25°C for 24 hours and wiped with ethanol. The test results of this sample are shown in Table 2.

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Comparative Example 5

[0099] A surface treating agent aqueous solution was prepared by diluting the reaction solution obtained in Synthesis Example 9 with water so that the concentration of its active component was 2% by weight. The solution was white turbid immediately after preparation. A glass plate of 70 mm x 150 mm x 3 mm thick was dipped in the solution for 5 minutes, air dried at 25°C for 24 hours and wiped with ethanol. The test results of this sample are shown in Table 2.

Comparative Example 6

[0100] A surface treating agent aqueous solution was prepared by diluting the reaction solution obtained in Synthesis Example 10 with water so that the concentration of its active component was 2% by weight. A glass plate of 70 mm x 150 mm x 3 mm thick was dipped in the solution for 5 minutes, air dried at 25°C for 24 hours and wiped with ethanol. The test results of this sample are shown in Table 2.

Table 2

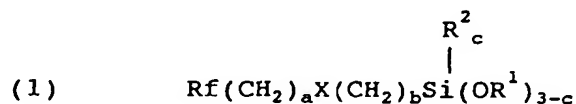
	Contact angle (°)		Contact angle (°) after boiling test		Contact angle (°) after abrasion test	
	Fresh	7 days	Fresh	7 days	Fresh	7 days
Example 8	105	105	98	97	100	99
Example 9	101	102	97	98	98	99
Example 10	104	105	97	99	96	96
Example 11	102	103	93	92	98	97
Example 12	101	102	91	89	90	90
Example 13	100	101	88	86	89	90
Example 14	103	101	96	94	97	97
Example 15	105	105	98	96	100	98
CE 4	80	<20	43	<20	40	<20
CE 5	94	82	62	58	48	41
CE 6	102	100	61	59	45	43

[0101] There have been described water-soluble surface treating agents which have good water solubility and shelf stability since water solubility is imparted to a fluoroalkyl group-containing silane compound itself. An aqueous solution of the agent is applied to glass and other substrates to impart water repellency and other good surface properties to the substrates, and these good properties were long-lasting.

[0102] Although some preferred embodiments have been described, many modifications and variations may be made thereto in the light of the above teachings.

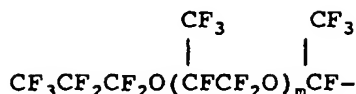
Claims

1. A water-soluble surface treating agent comprising as an active ingredient a reaction product of (A) fluoroalkyl group-containing alkoxysilane of the general formula (1):



wherein Rf is $\text{C}_n\text{F}_{2n+1}$ or a polyfluoroalkyl group represented by

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wherein n is an integer of 1 to 20 and m is an integer of at least 1, which may have at least one ether bond,

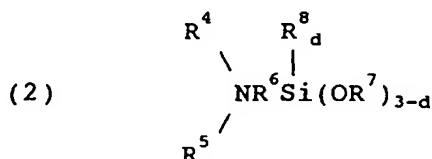
X is at least one linkage group selected from the class consisting of $-\text{CH}_2-$, $-\text{CH}_2\text{O}-$, $-\text{NR}^3-$, $-\text{CO}_2-$, $-\text{CONR}^3-$, $-\text{S}-$, $-\text{SO}_3-$, and $-\text{SO}_2\text{NR}^3-$ wherein R^3 are hydrogen atom or alkyl groups of 1 to 8 carbon atoms,

R^1 are alkyl groups having 1 to 4 carbon atoms,

R^2 are alkyl groups having 1 to 4 carbon atoms,

a is an integer of 0 to 3, b is an integer of 1 to 3, and c is equal to 0 or 1, and/or partial hydrolysate thereof

and
(B) amino group-containing alkoxysilane of the general formula (2):



wherein R^4 and R^5 are independently selected from the class consisting of hydrogen atom, alkyl groups having 1 to 15 carbon atoms, and aminoalkyl groups having 1 to 15 carbon atoms,

R^6 is a divalent hydrocarbon group having 1 to 18 carbon atoms,

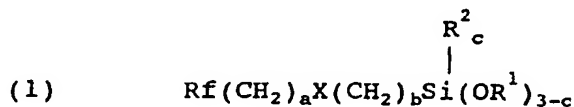
R^7 are alkyl groups having 1 to 4 carbon atoms,

R^8 are alkyl groups having 1 to 4 carbon atoms, and

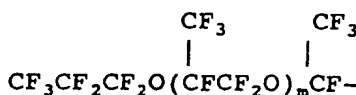
d is equal to 0 or 1, and/or a partial hydrolysate

thereof, and wherein the reaction product is obtained by reacting components (B) and (A) in a molar ratio of from 0.5/1.0 to 20.0/1.0.

2. An agent of claim 1 comprising 0.1 to 10% by weight of the reaction product and 99.9 to 90% by weight of water.
3. A water-soluble surface treating agent comprising as a main ingredient a reaction product of (A) fluoroalkyl group-containing alkoxysilane of the general formula (1):



wherein Rf is $\text{C}_n\text{F}_{2n+1}$ or a polyfluoroalkyl group represented by



wherein n is an integer of 1 to 20 and m is an integer of at least 1, which may have at least one ether bond,

X is at least one linkage group selected from the class consisting of $-\text{CH}_2-$, $-\text{CH}_2\text{O}-$, $-\text{NR}^3-$, $-\text{CO}_2-$, $-\text{CONR}^3-$, $-\text{S}-$, $-\text{SO}_3-$, and $-\text{SO}_2\text{NR}^3-$ wherein R^3 are hydrogen atom or alkyl groups of 1 to 8 carbon atoms

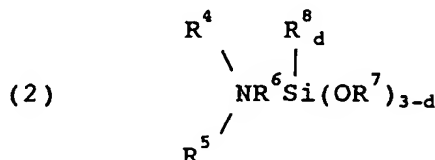
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R¹ are alkyl groups having 1 to 4 carbon atoms,

R² are alkyl groups having 1 to 4 carbon atoms,

a is an integer of 0 to 3, b is an integer of 1 to 3, and c is equal to 0 or 1, and/or a partial hydrolysate thereof,

(B) amino group-containing alkoxyasilane of the general formula (2):



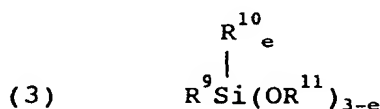
wherein R⁴ and R⁵ are independently selected from the class consisting of hydrogen atom, alkyl groups having 1 to 15 carbon atoms, and aminoalkyl groups having 1 to 15 carbon atoms,

R⁶ is a divalent hydrocarbon group having 1 to 18 carbon atoms,

R⁷ are alkyl groups having 1 to 4 carbon atoms,

R⁸ are alkyl groups having 1 to 4 carbon atoms, and d is equal to 0 or 1, and/or a partial hydrolysate thereof, and

(C) alkyl group-containing alkoxyasilane of the general formula (3):



wherein R⁹ is a monovalent hydrocarbon group having 1 to 10 carbon atoms,

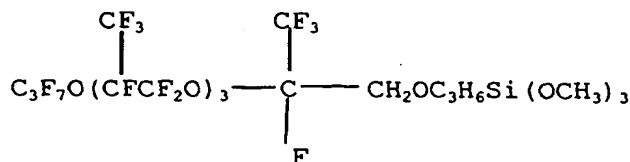
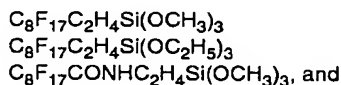
R¹⁰ is an alkyl group having 1 to 4 carbon atoms,

R¹¹ is an alkyl group having 1 to 4 carbon atoms,

and e is equal to 0 or 1 and/or a partial hydrolysate thereof,

and wherein the reaction product is obtained by reacting components (A) and (C) in a molar ratio (C) / (A) of from 0.05/1 to 0.5/1 and further reacting them with component (B) in a molar ratio (B) / (A + C) of from 0.5/1 to 20/1.

4. An agent of claim 4 comprising 0.1 to 10% by weight of the reaction product and 99.9 to 90% by weight of water.
5. A method of making a surface treating agent according to claim 1, by reacting said components (A) and (B), or a surface treating agent according to claim 3, by reacting said components (A), (B) and (C).
6. The agent of claim 1 or claim 3 wherein the fluoroalkyl group-containing alkoxyasilane is selected from the group consisting of



7. The agent of claim 1 or claim 3 wherein the amino group-containing alkoxyasilane is selected from the group consisting of:

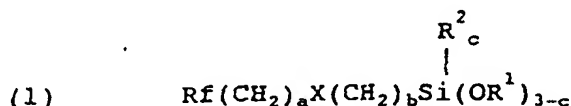
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N-(2-aminoethyl)-3-aminopropyl trimethoxysilane,
N-(2-aminoethyl)-3-aminopropylmethyldimethoxysilane and 3-aminopropyl trimethoxysilane

8. The agent of claim 1 wherein the reaction product is obtained by co-hydrolysis and condensation of (A) and (B) in the presence of an organic or inorganic acid.
9. The agent of claim 1 wherein the reaction product is obtained by effecting partial hydrolysis of (A) in the presence of an organic or inorganic acid and then reacting the obtained partial hydrolysis product with (B).
10. The agent of claim 9 wherein the organic or inorganic acid is hydrochloric, sulphuric, methanesulphonic, formic, acetic, propionic, citric, oxalic, maleic acid or a mixture thereof.
11. The agent of claim 9 wherein the organic or inorganic acid is used in an amount of 5 to 400 parts by weight per 100 parts by weight of (A).
12. The agent of claim 9 wherein the partial hydrolysis is effected in an amount of 1.0 to 3.0 mol of water per mol of (A).
13. The agent of claim 9 wherein the partial hydrolysis is conducted at 10° to 100°C for 1 to 3 hours.
14. The agent of claim 9 wherein the reaction of the partial hydrolysis product with (B) is conducted at 60° to 100°C for 1 to 3 hours.
15. The agent of claim 3 wherein the alkyl group-containing alkoxy silane is selected from the group consisting of:
 $C_{10}H_{21}Si(OCH_3)_3$, $C_{10}H_{21}Si(CH_3)(OCH_3)_2$, $(CH_3)_2Si(OCH_3)_2$ and $(CH_3)_2Si(OC_2H_5)_2$
16. The agent of claim 3 wherein the reaction product is obtained by effecting partial hydrolysis of (A) and (C) in the presence of an organic or inorganic acid and then reacting the obtained partial hydrolysis product with (B).
17. The agent of claim 16 wherein the organic or inorganic acid is hydrochloric, sulphuric, methanesulphonic, formic, acetic, propionic, citric, oxalic, maleic acid or a mixture thereof.
18. The agent of claim 16 wherein the organic or inorganic acid is used in an amount of 30 to 400 parts by weight per 100 parts by weight of (A) and (C) combined.
19. The agent of claim 16 wherein the partial hydrolysis is effected in an amount of 1.0 to 3.0 mol of water per mol of (A) and (C) combined.
20. The agent of claim 16 wherein the partial hydrolysis is conducted at 10° to 100°C for 1 to 3 hours.
21. The agent of claim 6 wherein the reaction of the partial hydrolysis product with (B) is conducted at 60° to 100°C for 1 to 3 hours.
22. to Use of an agent according to any one of claims 1 to 4 to treat a surface of a substrate.

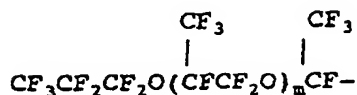
Patentansprüche

1. Wasserlösliches Oberflächen-Behandlungsmittel, umfassend als Aktivbestandteil ein Reaktionsprodukt aus
(A) Fluoralkylgruppe enthaltendem Alkoxysilan der allgemeinen Formel (1).



worin $R_f = C_nF_{2n+1}$ oder eine durch

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dargestellte Polyfluoralkylgruppe ist,
 worin n eine ganze Zahl von 1 bis 20 ist und m eine ganze Zahl von zumindest 1 ist, die zumindest eine
 Etherbindung aufweisen kann,

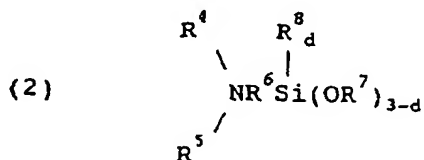
X zumindest eine Bindungsgruppe ist, die aus der aus -CH₂-, -CH₂O-, -NR³-, -CO₂-, -CONR³-, -S-, -SO₃-
 und -SO₂NR³- bestehenden Klasse ausgewählt ist, worin die Reste R³ Wasserstoffatome oder Alkylgrup-
 pen mit 1 bis 8 Kohlenstoffatomen sind,

R¹ eine Alkylgruppe mit 1 bis 4 Kohlenstoffatomen ist,

R² eine Alkylgruppe mit 1 bis 4 Kohlenstoffatomen ist,

a eine ganze Zahl von 0 bis 3 ist, b eine ganze Zahl von 1 bis 3 ist, und c = 0 oder 1 ist, und/oder einem
 partiellen Hydrolysat davon sowie

(B) Aminogruppe enthaltendem Alkoxysilan der allgemeinen Formel (2):



worin R⁴ und R⁵ unabhängig voneinander aus der aus Wasserstoffatom, Alkylgruppen mit 1 bis 15 Kohlen-
 stoffatomen und Aminoalkylgruppen mit 1 bis 15 Kohlenstoffatomen bestehenden Klasse ausgewählt sind,

R⁶ eine zweiwertige Kohlenwasserstoffgruppe mit 1 bis 18 Kohlenstoffatomen ist,

die Reste R⁷ Alkylgruppen mit 1 bis 4 Kohlenstoffatomen sind,

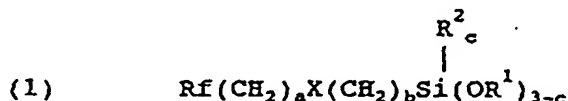
die Reste R⁸ Alkylgruppen mit 1 bis 4 Kohlenstoffatomen sind, und

d = 0 oder ist, und/oder einem partiellen Hydrolysat davon ist, wobei das Reaktionsprodukt durch Umset-
 zen der Komponenten (B) und (A) in einem Molverhältnis von 0,5:1,0 bis 20,0:1,0 erhalten wird.

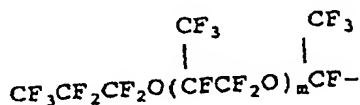
2. Mittel nach Anspruch 1, das 0,1 bis 10 Gew.-% des Reaktionsprodukts und 99,9 bis 90 Gew.-% Wasser enthält.

3. Wasserlösliches Oberflächen-Behandlungsmittel, umfassend als Hauptbestandteil ein Reaktionsprodukt aus

(A) Fluoralkylgruppe enthaltendem Alkoxysilan der allgemeinen Formel (1):



worin R_f C_nF_{2n+1} oder eine durch



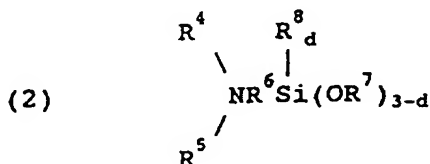
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dargestellte Polyfluoralkylgruppe ist,
 worin n eine ganze Zahl von 1 bis 20 ist und m eine ganze Zahl von zumindest 1 ist, die zumindest eine
 Etherbindung aufweisen kann,

5 X zumindest eine Bindungsgruppe ist, die aus der aus $-\text{CH}_2-$, $-\text{CH}_2\text{O}-$, $-\text{NR}^3-$, $-\text{CO}_2-$, $-\text{CONR}^3-$, $-\text{S}-$, $-\text{SO}_3-$
 und $-\text{SO}_2\text{NR}^3-$ bestehenden Klasse ausgewählt ist, worin die Reste R^3 Wasserstoffatome oder Alkylgrup-
 pen mit 1 bis 8 Kohlenstoffatomen sind,
 die Reste R^1 Alkylgruppen mit 1 bis 4 Kohlenstoffatomen sind,
 die Reste R^2 Alkylgruppen mit 1 bis 4 Kohlenstoffatomen sind,
 10 a eine ganze Zahl von 0 bis 3 ist, b eine ganze Zahl von 1 bis 3 ist und c = 0 oder 1 ist, und/oder einem
 partiellen Hydrolysat davon,

(B) Aminogruppe enthaltendem Alkoxysilan der allgemeinen Formel (2):

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worin R^4 und R^5 unabhängig voneinander aus der aus Wasserstoffatom, Alkylgruppen mit 1 bis 15 Kohlen-
 25 stoffatomen und Aminoalkylgruppen mit 1 bis 15 Kohlenstoffatomen bestehenden Klasse ausgewählt sind,

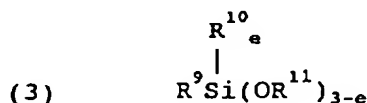
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R^6 eine zweiwertige Kohlenwasserstoffgruppe mit 1 bis 18 Kohlenstoffatomen ist,
 die Reste R^7 Alkylgruppen mit 1 bis 4 Kohlenstoffatomen sind,
 die Reste R^8 Alkylgruppen mit 1 bis 4 Kohlenstoffatomen sind, und
 30 d = 0 oder 1 ist, und/oder einem partiellen Hydrolysat davon sowie

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(C) Alkylgruppe enthaltendem Alkoxysilan der allgemeinen Formel (3):

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worin R^9 eine einwertige Kohlenwasserstoffgruppe mit 1 bis 10 Kohlenstoffatomen ist,

R^{10} eine Alkylgruppe mit 1 bis 4 Kohlenstoffatomen ist,

R^{11} eine Alkylgruppe mit 1 bis 4 Kohlenstoffatomen ist und

e = 0 oder 1 ist, und/oder einem partiellen Hydrolysat davon ist, wobei das Reaktionsprodukt erhalten
 45 wird, indem die Komponenten (A) und (C) in einem Molverhältnis (C) : (A) = 0,05:1 bis 0,5:1 umgesetzt
 werden und sie weiters mit Komponente (B) in einem Molverhältnis (B) : (A + C) = 0,5:1 bis 20:1 umgesetzt
 werden.

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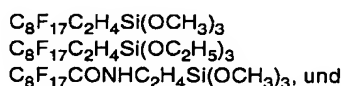
4. Mittel nach Anspruch 3, umfassend 0,1 bis 10 Gew.-% des Reaktionsprodukts und 99,9 bis 90 Gew.-% Wasser.

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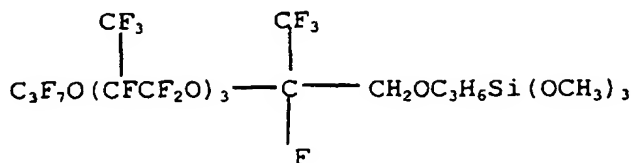
5. Verfahren zur Herstellung eines Oberflächen-Behandlungsmittels nach Anspruch 1 durch Umsetzen der Kompo-
 nenten (A) und (B), oder eines Oberflächen-Behandlungsmittels nach Anspruch 3, durch Umsetzen der Kompo-
 nenten (A), (B) und (C).

6. Mittel nach Anspruch 1 oder 3, worin das Fluoralkylgruppe enthaltende Alkoxysilan aus der aus

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bestehenden Gruppe ausgewählt ist.

7. Mittel nach Anspruch 1 oder 3, worin das Aminogruppe enthaltende Alkoxysilan aus der aus

N-(2-Aminoethyl)-3-aminopropyltrimethoxysilan,
N-(2-Aminoethyl)-3-aminopropylmethyldimethoxysilan und
3-Aminopropyltrimethoxysilan bestehenden Gruppe ausgewählt ist.

8. Mittel nach Anspruch 1, worin das Reaktionsprodukt durch Co-Hydrolyse und Kondensation von (A) und (B) in Gegenwart einer organischen oder anorganischen Säure erhalten wird.

9. Mittel nach Anspruch 1, worin das Reaktionsprodukt erhalten wird, indem partielle Hydrolyse von (A) in Gegenwart einer organischen oder anorganischen Säure bewirkt und anschließend das erhaltene Produkt der partiellen Hydrolyse mit (B) umgesetzt wird.

10. Mittel nach Anspruch 9, worin die organische oder anorganische Säure Salzsäure, Schwefelsäure, Methansulfonsäure, Ameisensäure, Essigsäure, Propionsäure, Zitronensäure, Oxalsäure, Maleinsäure oder ein Gemisch davon ist.

11. Mittel nach Anspruch 9, worin die organische oder anorganische Säure in einer Menge von 5 bis 400 Gewichtsteilen pro 100 Gewichtsteile von (A) eingesetzt wird.

12. Mittel nach Anspruch 9, worin die partielle Hydrolyse in einer Menge von 1,0 bis 3,0 Mol Wasser pro Mol (A) durchgeführt wird.

13. Mittel nach Anspruch 9, worin die partielle Hydrolyse bei 10 bis 100 °C für 1 bis 3 h durchgeführt wird.

14. Mittel nach Anspruch 9, worin die Reaktion des Produktes der partiellen Hydrolyse mit (B) bei 60 bis 100 °C für 1 bis 3 h durchgeführt wird.

15. Mittel nach Anspruch 3, worin das Alkylgruppe enthaltende Alkoxysilan aus der aus $\text{C}_{10}\text{H}_{21}\text{Si}(\text{OCH}_3)_3$, $\text{C}_{10}\text{H}_{21}\text{Si}(\text{CH}_3)(\text{OCH}_3)_2$, $(\text{CH}_3)_2\text{Si}(\text{OCH}_3)_2$ und $(\text{CH}_3)_2\text{Si}(\text{OC}_2\text{H}_5)_2$ bestehenden Gruppe ausgewählt ist.

16. Mittel nach Anspruch 3, worin das Reaktionsprodukt erhalten wird, indem partielle Hydrolyse von (A) und (C) in Gegenwart einer organischen oder anorganischen Säure bewirkt und anschließend das Produkt der partiellen Hydrolyse mit (B) umgesetzt wird.

17. Mittel nach Anspruch 6, worin die organische oder anorganische Säure Salzsäure, Schwefelsäure, Methansulfonsäure, Ameisensäure, Essigsäure, Propionsäure, Zitronensäure, Oxalsäure, Maleinsäure oder ein Gemisch davon ist.

18. Mittel nach Anspruch 16, worin die organische oder anorganische Säure in einer Menge von 30 bis 400 Gewichtsteilen pro 100 Gewichtsteile der Kombination von (A) und (C) eingesetzt wird.

19. Mittel nach Anspruch 16, worin die partielle Hydrolyse in einer Menge von 1,0 bis 3,0 Mol Wasser pro Mol der Kombination von (A) und (C) durchgeführt wird.

20. Mittel nach Anspruch 16, worin die partielle Hydrolyse bei 10 bis 100 °C für 1 bis 3 h durchgeführt wird.

21. Mittel nach Anspruch 6, worin die Reaktion des Produktes der partiellen Hydrolyse mit (B) bei 60 bis 100 °C für 1

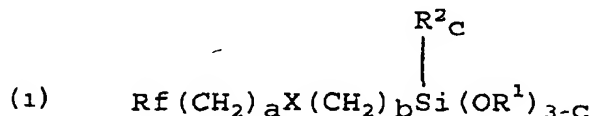
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bis 3 h durchgeführt wird.

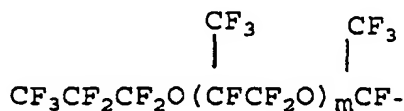
22. Verwendung eines Mittels nach einem der Ansprüche 1 bis 4 zur Behandlung einer Oberfläche eines Substrats.

Revendications

1. Agent de traitement de surface soluble dans l'eau comprenant, comme ingrédient actif, un produit réactionnel de (A) un alcoxysilane comprenant un groupe fluoroalkyle de la formule générale (1) :



où R^f est C_nF_{2n+1} ou un groupe polyfluoroalkyle représenté par



où n est un entier de 1 à 20 et m est un entier d'au moins 1, qui peut avoir au moins une liaison éther,

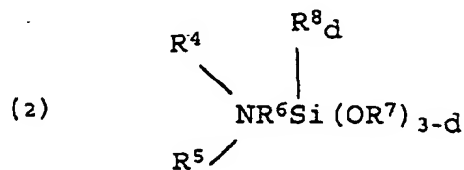
X est au moins un groupe d'enchaînement sélectionné dans la classe consistant en -CH₂-, -CH₂O-, -NR³-, -CO₂-, -COMR³-, -S-, -SO₃-, et -SO₂NR³-, où R³ sont un atome d'hydrogène ou des groupes alkyle de 1 à 8 atomes de carbone,

R¹ sont des groupes alkyle ayant 1 à 4 atomes de carbone,

R² sont des groupes alkyle ayant 1 à 4 atomes de carbone,

a est un entier de 0 à 3, b est un entier de 1 à 3 et c est égal à 0 ou 1, et/ou son hydrolysate partiel, et

(B) un alcoxysilane contenant un groupe amine de la formule générale (2) :



où R⁴ et R⁵ sont indépendamment sélectionnés dans la classe consistant en atome d'hydrogène, groupes alkyle ayant 1 à 15 atomes de carbone et groupes aminoalkyle ayant 1 à 15 atomes de carbone,

R⁶ est un groupe hydrocarbure divalent ayant 1 à 18 atomes de carbone,

R⁷ sont des groupes alkyle ayant 1 à 4 atomes de carbone,

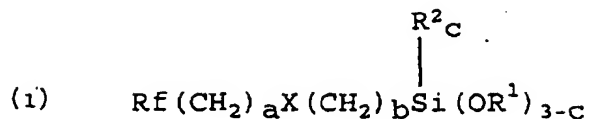
R⁸ sont des groupes alkyle ayant 1 à 4 atomes de carbone, et

d est égal à 0 ou 1, et/ou son hydrolysate partiel et où le produit réactionnel est obtenu par réaction des composants (B) et (A) à un rapport molaire de 0,5/1,0 à 20,0/1,0.

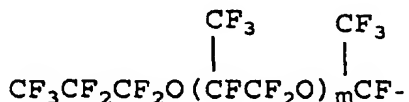
2. Agent de la revendication 1, comprenant 0,1 à 10% en poids du produit réactionnel et 99,9 à 90% en poids d'eau.

3. Agent de traitement de surface soluble dans l'eau comprenant, comme ingrédient principal, un produit réactionnel de (A) un alcoxysilane contenant un groupe fluoroalkyle de la formule générale (1) :

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où R^f est C_nP_{2n+1} ou un groupe polyfluoroalkyle représenté par



où n est un entier de 1 à 20 et m est un entier d'au moins 1, qui peut avoir au moins une liaison éther,

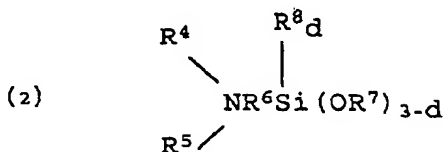
X est au moins un groupe d'enchaînement sélectionné dans la classe consistant en -CH₂-, -CH₂O-, -NR³-, -CO₂-, -CONR³-, -S-, -SO₃-, et -SO₂NR³-, où R³ sont un atome d'hydrogène ou des groupes alkyle de 1 à 8 atomes de carbone,

R¹ sont des groupes alkyle ayant 1 à 4 atomes de carbone,

R² sont des groupes alkyle ayant 1 à 4 atomes de carbone,

a est un entier de 0 à 3, b est un entier de 1 à 3 et c est égal à 0 ou 1, et/ou son hydrolysate partiel, et

(B) un alcoxysilane contenant un groupe amine de la formule générale (2) :



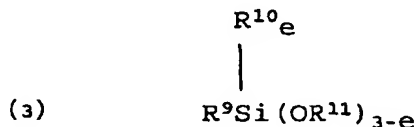
où R⁴ et R⁵ sont indépendamment sélectionnés dans la classe consistant en un atome d'hydrogène, des groupes alkyle ayant 1 à 15 atomes de carbone et des groupes aminoalkyle ayant 1 à 15 atomes de carbone, R⁶ est un groupe hydrocarbure divalent ayant 1 à 18 atomes de carbone,

R⁷ sont des groupes alkyle ayant 1 à 4 atomes de carbone,

R⁸ sont des groupes alkyle ayant 1 à 4 atomes de carbone, et

d est égal à 0 ou 1, et/ou leur hydrolysate partiel, et

(C) un alcoxysilane contenant un groupe alkyle de la formule générale



ou R⁹ est un groupe hydrocarbure monovalent ayant 1 à 10 atomes de carbones,

R¹⁰ est un groupe alkyle ayant 1 à 4 atomes de carbone,

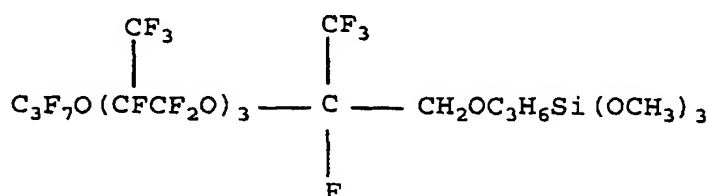
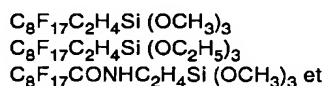
R¹¹ est un groupe alkyle ayant 1 à 4 atomes de carbone,

et e est égal à 0 ou 1 et/ou leur hydrolysate partiel,

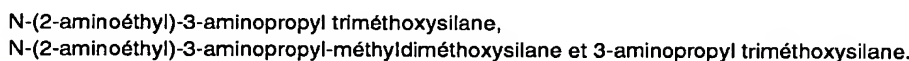
et où le produit réactionnel est obtenu par réaction des composant (A) et (C) à un rapport molaire de (C)/(A) de 0,05/1 à 0,5/1 et de plus leur réaction avec le composant (B) à un rapport molaire (B)/(A+C) de 0,5/1 à 20/1.

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4. Agent de la revendication 4, comprenant 0,1 à 10% en poids du produit réactionnel et 99,9 à 90% en poids d'eau.
5. Méthode de production d'un agent de traitement de surface selon la revendication 1 par réaction desdits composant (A) et (B) ou d'un agent de traitement de surface selon la revendication 3 par réaction desdits composant (A), (B) et (C).
6. Agent de la revendication 1 ou de la revendication 3, où l'alcoxysilane contenant un groupe fluoroalkyle est sélectionné dans le groupe consistant en



7. Agent de la revendication 1 ou de la revendication 3, où l'alcoxysilane contenant un groupe amine est sélectionné dans le groupe consistant en :



8. Agent de la revendication 1, où le produit réactionnel est obtenu par co-hydrolyse et condensation de (A) et (B) en présence d'un acide organique ou inorganique.
9. Agent de la revendication 1, où le produit réactionnel est obtenu en effectuant l'hydrolyse partielle de (A) en présence d'un acide organique ou inorganique puis en faisant réagir le produit d'hydrolyse partielle obtenu avec (B).
10. Agent de la revendication 9, où l'acide organique ou inorganique est l'acide chlorhydrique, sulfurique, méthane-sulfonique, formique, acétique, propionique, citrique, oxallique, maléique ou un mélange.
11. Agent de la revendication 9, où l'acide organique ou inorganique est utilisé en une quantité de 5 à 400 parties en poids pour 100 parties en poids de (A).
12. Agent de la revendication 9, où l'hydrolyse partielle est effectuée en une quantité de 1,0 à 3,0 moles d'eau par mole de (A).
13. Agent de la revendication 9, où l'hydrolyse partielle est entreprise à 10° jusqu'à 100°C pendant 1 à 3 heures.
14. Agent de la revendication 9, où la réaction du produit d'hydrolyse partielle avec (B) est entreprise à 60° jusqu'à 100°C pendant 1 à 3 heures.
15. Agent de la revendication 3, où l'alcoxysilane contenant un groupe alkyle est sélectionné dans le groupe consistant en :
- $$\text{C}_{10}\text{H}_{21}\text{Si}(\text{OCH}_3)_3, \text{C}_{10}\text{H}_{21}\text{Si}(\text{CH}_3)(\text{OCH}_3)_2, (\text{CH}_3)_2\text{Si}(\text{OCH}_3)_2 \text{ et } (\text{CH}_3)_3\text{Si}(\text{OC}_2\text{H}_5)_2.$$
16. Agent de la revendication 3, où le produit réactionnel est obtenu en effectuant l'hydrolyse partielle de (A) et (C) en présence d'un acide organique ou inorganique puis en faisant réagir le produit d'hydrolyse partielle obtenu avec (B).

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17. Agent de la revendication 16, où l'acide organique ou inorganique est l'acide chlorhydrique, sulfurique, méthane-sulfonique, formique, acétique, propionique, citrique, oxalique, maléique ou un mélange.
- 5 18. Agent de la revendication 16, où l'acide organique ou inorganique est utilisé en une quantité de 30 à 400 parties en poids pour 100 parties en poids de (A) et (C) combinés.
19. Agent de la revendication 16, où l'hydrolyse partielle est effectuée en une quantité de 1,0 à 3,0 moles d'eau par mole de (A) et (C) combinés.
- 10 20. Agent de la revendication 16, où l'hydrolyse partielle est entreprise à 10° jusqu'à 100°C pendant 1 à 3 heures.
21. Agent de la revendication 6, où la réaction du produit d'hydrolyse partielle avec (B) est entreprise à 60° jusqu'à 100°C pendant 1 à 3 heures.
- 15 22. Utilisation d'un agent selon l'une quelconque des revendications 1 à 4 pour traiter une surface d'un substrat.

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